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A Large-Sample Extractor for Determining Organic Contaminants in the Great Lakes

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TECHNICAL BULLETIN NO. 157

**INLAND WATERS DIRECTORATE
ONTARIO REGION
WATER QUALITY BRANCH
BURLINGTON, ONTARIO, 1988**

(Disponible en français sur demande)

Published by authority of
the Minister of the Environment

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Cat. No. En 38-503/157E

ISBN 0-662-16078-9

Contents

	Page
ABSTRACT	v
RÉSUMÉ	v
EXECUTIVE SUMMARY	vii
INTRODUCTION	1
EXPERIMENTAL	1
Apparatus	1
Reagents	2
Procedure	2
RESULTS AND DISCUSSION	6
ACKNOWLEDGMENTS	12
REFERENCES	12
APPENDIX A. Percent recoveries of surrogate standards for each station, by lake.	13
APPENDIX B. Ratios found in extracts, normalized to endrin ketone	19

Tables

1. Sampling dates for organic contaminants cruises conducted on the Great Lakes.	2
2. Contents of the surrogate standard solutions, in methanol.	3
3. 1986 Great Lakes organics results: surrogate standard spike recoveries.	6

Illustrations

Figure 1. Flow diagram of equipment.	2
Figure 2. Extractor.	2
Figure 3. Separator trap.	3
Figure 4. Water heating tube.	3
Figure 5. 1986 Organic contaminant sampling sites on Lake Superior.	4
Figure 6. 1986 Organic contaminant sampling sites on Lake Huron - Georgian Bay. ...	4
Figure 7. 1986 Organic contaminant sampling sites on Lake Erie.	5
Figure 8. 1986 Organic contaminant sampling sites on Lake Ontario	5
Figure 9. Lake Superior: centrifuged vs. ambient duplicates	7
Figure 10. Lake Huron: centrifuged vs. ambient duplicates	8
Figure 11. Georgian Bay: centrifuged vs. ambient duplicates	9
Figure 12. Lake Erie: centrifuged vs. ambient duplicates	10
Figure 13. Lake Ontario: centrifuged vs. ambient duplicates.	11



Abstract

The construction and operation of two large-sample extractors onboard the CSS *Limnos* are described. They can extract water at up to $1 \text{ L} \cdot \text{min}^{-1}$ and were used to extract water samples of approximately 50-L volume with dichloromethane during the monitoring cruises on lakes Erie, Huron, Ontario and Superior in early 1986. Both whole water and clarified water were extracted. The dichloromethane extracts were later analyzed for organochlorines, chlorobenzenes, polychlorinated biphenyls, and polynuclear aromatics by the National Water Quality Laboratory in Burlington, Ontario. A solution containing surrogate standards was continuously added at a fixed rate to the water being extracted. The recoveries of these surrogates provide a continuous measure of the extraction efficiency and reproducibility of the analytical process, and confirm that the processes used are valid.

Résumé

On décrit la construction et le fonctionnement de deux extracteurs à grand volume, utilisés à bord du *Limnos*. Ils peuvent utiliser jusqu'à $1 \text{ L} \cdot \text{min}^{-1}$ d'eau pour l'extraction. Ils ont été utilisés pour extraire des échantillons d'eau d'environ 50 L chacun pour l'extraction par du dichlorométhane au cours de missions de surveillance sur les lacs Érié, Huron, Ontario et Supérieur au début de 1986. Des échantillons d'eau non filtrée et d'eau décantée ont servi à l'extraction. Les extraits au dichlorométhane ont ensuite été analysés par le Laboratoire national de la qualité des eaux à Burlington (Ontario) pour établir les teneurs en composés organochlorés, en chlorobenzènes, en polychlorobiphényles et en hydrocarbures aromatiques polycycliques. Une solution contenant des étalons simulés était continuellement ajoutée à l'eau, à un débit constant pendant l'extraction. La récupération de ces solutions étalons permet une mesure continue de l'efficacité de l'extraction et de la reproductibilité du procédé analytique et confirme la validité des procédés utilisés.

Executive Summary

Two large-sample extractors were used onboard the CSS *Limnos* during the Great Lakes surveillance cruises in 1986 to extract samples for organic contaminants analysis. The results show that this technique is valid for determining levels of organic contaminants in the waters of the Great Lakes.



A Large-Sample Extractor for Determining Organic Contaminants in the Great Lakes

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INTRODUCTION

There is a great need for monitoring the levels of organics in waters of the Great Lakes. The materials of interest, however, occur at low concentrations, and with the use of standard analytical methodology and the standard sampling technique of collection in bottles for later analysis in the laboratory, most of the organics are found to be not detectable. One approach to greater sensitivity is the use of larger samples combined with pre-concentration at the sampling site. Pre-concentration processes such as adsorption on urethane foam or on resins, and solvent extractions have been used with varying degrees of success.

In the Ontario Region of the Water Quality Branch the APLE sampler was developed (McCrea and Fischer, 1985). The APLE (aqueous phase liquid-liquid extractor) sampler is based on a 45-gallon drum in which 200 L of water is extracted with 8 L dichloromethane using a centrifugal pump and solvent spray bar for the agitation. Use of this equipment has shown that (1) with a large sample volume, the organics of interest can be determined with standard analytical techniques and (2) essentially complete extraction of the organic materials can be obtained with a single-stage process.

In cooperation with the Water Quality Branch, a continuous-flow extractor has recently been developed in the National Water Research Institute (NWRI), Burlington. The extractor facilitates extraction of very large samples in the field. It is basically a mixer-settler, extracting water at up to $1 \text{ L} \cdot \text{min}^{-1}$. The water is further extracted in a packed column by the clean solvent used to make up the solvent lost by solution in the effluent water. The design characteristics of the equipment have been described by Goulden and Anthony (1985). Two prototypes were used on the CSS *Limnos* in September 1985, to confirm the applicability of this type of equipment to a shipboard laboratory and to determine suitable operating procedures. Two field units were built in early 1986 and used during the surveillance cruises on lakes Erie, Huron, Ontario and Superior. The results obtained from these cruises show that the technique is viable and appears to provide a valid measure of the organics in Great Lakes water.

EXPERIMENTAL

Apparatus

Figure 1 shows a flow diagram of the equipment. The extraction equipment is similar to that described by Goulden and Anthony (1985), the differences being that the solvent make-up is added with a metering pump; the separator trap is of improved design; provision is made to heat the incoming water; and surrogate standards are added with a metering pump. Figure 2 shows the extractor in detail. Figures 3 and 4 show the separator trap and the water heating tube, respectively, in detail.

The stirrer motor is type RZR50 made by Caframo in Warton, Ontario (CANLAB No. S-7995-100). The stirrer is a four-blade turbine type (CANLAB No. S8185-15) with the ends trimmed (so that it will fit through the neck of the mixing chamber) and the blades turned through approximately 45° from the vertical. The stirrer is mounted on a stand with a 20-mm diameter rod (CANLAB No. S7996-8). The rest of the equipment is hung from a 13-mm diameter rod which is fixed beside the 20-mm rod, about 70 mm from it. The bottom of the smaller rod is fixed in a threaded hole drilled in the base of the stand. The upper end is held in an aluminum spacer block. The extractor is held by two chain clamps (CANLAB No. C-6008) which hold a sheet metal sleeve with a 3 mm thick Teflon liner around the mixing chamber. The rest of the glassware is supported by jaw-style laboratory clamps. The Vycor heater (CANLAB No. H-1970-1M) is controlled by a variable rheostat set to heat the water to approximately 20°C to 22°C before it enters the mixing chamber. The pumps are manufactured by Fluid Metering Inc., Oyster Bay, N.Y. The water supply pump, solvent make-up pump, and spiking pump are models RPD-2CSC, RPG-50-2CSC and RPG-6-1CSC, respectively. All connections are made with glass or Teflon tubing and stainless steel fittings. To overcome the water-hammer effect from the pump, small vertical closed-end glass tubes are fitted to the water supply pump inlet and outlet. The stand is bolted to a piece of plywood, to which the pumps are also attached. The plywood is bolted to the bench in the ship laboratory.

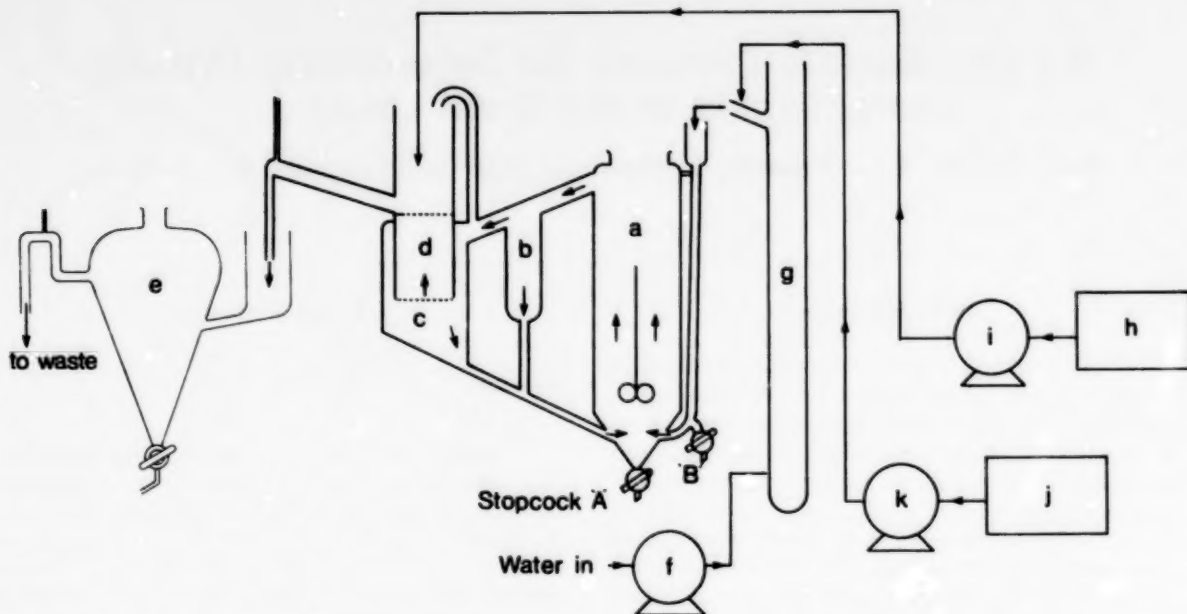


Figure 1. Flow diagram of equipment; a - mixing chamber; b - first settling chamber; c - second settling chamber; d - packed column; e - separator trap; f - metering pump-water; g - heater tube; h - solvent bottle; i - solvent make-up pump; j - surrogate standards bottle; k - "spiking" pump.

Reagents

Reagent-grade water for carrying out blank determinations was prepared by passing distilled water through a Milli Q-2 cartridge system (Millipore Corp.).

Procedure

Preliminary data on contaminant levels in the Great Lakes (Chan, 1984; Biberhofer and Stevens, 1987; Neilson *et al.*, 1986) suggested the requirement to process sample volumes of approximately 50 L in order to achieve detectable contaminant levels in the final extracts for analysis. The sampling schedule is outlined in Table 1; 44-L samples of water were collected on lakes Ontario and Erie and 66-L samples on lakes Huron and Superior.

Table 1. Sampling Dates for Organic Contaminants Cruises Conducted on the Great Lakes

	Sampling period
Lake Ontario	86-04-14 to 86-04-18
Lake Erie	86-04-28 to 86-05-02
Lake Huron - Georgian Bay	86-05-03 to 86-05-12
Lake Superior	86-05-12 to 86-05-19

The stations sampled are shown in Figures 5 to 8. A March submersible pump was employed with Teflon-lined, stainless steel-braided tubing to collect samples into 22-L glass carboys. All sampling was conducted from the windward side of the ship at a depth of 1 m. Centrifuged

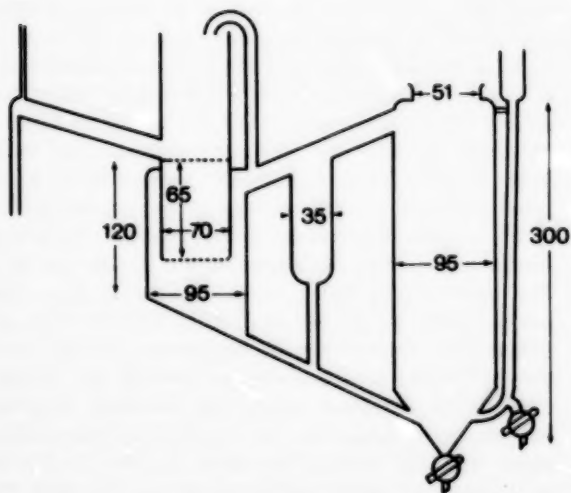


Figure 2. Extractor.

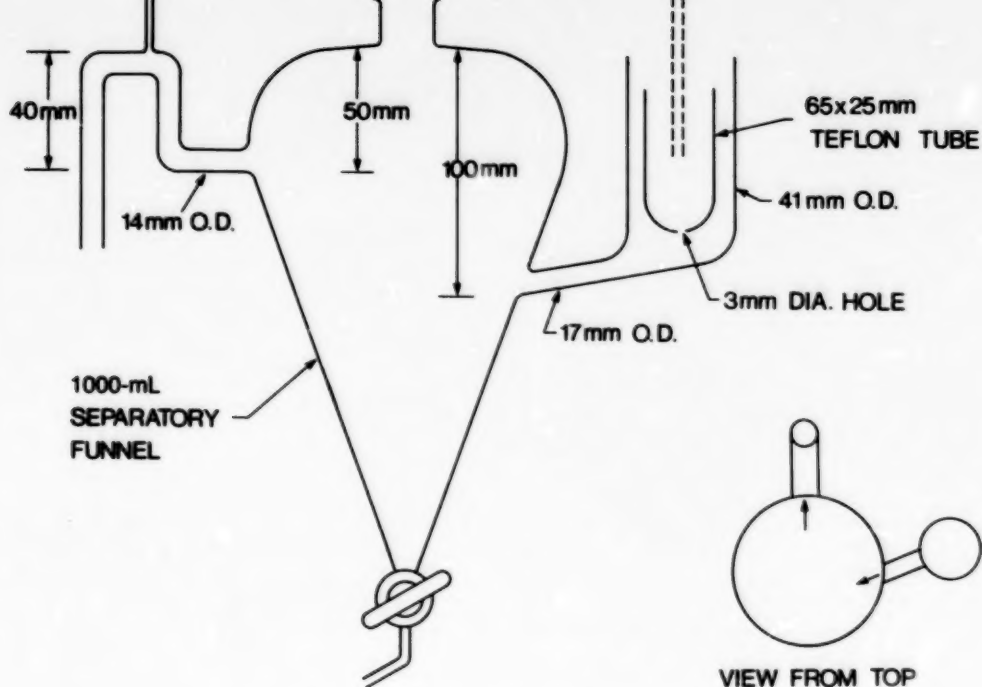


Figure 3. Separator trap.

samples were obtained using a similar setup, with the sample water being passed through a Westfalia centrifuge at a rate of $6 \text{ L} \cdot \text{min}^{-1}$. Centrifuged and ambient duplicates were collected at stations s002 and s031 on Lake Superior; h029 and h095 on Lake Huron; g033 on Georgian Bay; e221 and e357 on Lake Erie; and o041 and o081 on Lake Ontario.

Extraction of the water was started immediately. Initially, 200 mL of glass-distilled (Burdick and Jackson) dichloromethane was pumped into the mixing chamber, the stirrer started, and then the solvent pump rate re-established to sustain the level of solvent. (Periodically throughout the extraction the stirrer was stopped and the solvent level in the mixing chamber checked.) A glass wand, inserted into the end of the Teflon water feed line, was submerged into the carboy and the water feed pump started and

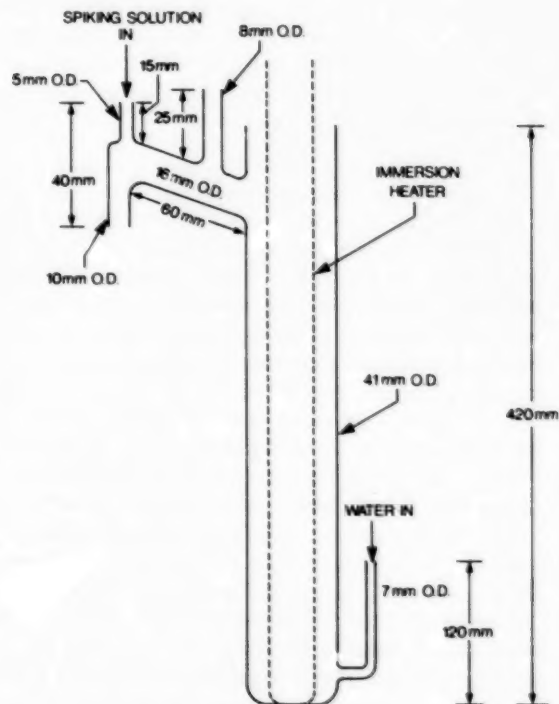


Figure 4. Water heating tube.

Table 2. Contents of the Surrogate Standard Solutions, in Methanol ($\mu\text{g} \cdot \text{L}^{-1}$)

Parameter	
1,3-Dibromobenzene (DBB)	1.028
1,3,5-Tribromobenzene (TBB)	0.408
1,2,4,5-Tetrabromobenzene (TeBB)	0.442
2,3,5,6-Tetrachlorobiphenyl (TCBP)	0.446
Endrin ketone (END-KETO)	0.10



Figure 5. 1986 Organic contaminant sampling sites on Lake Superior.

operated at a rate of 600 to 1000 mL·min⁻¹, depending on the sample. The surrogate standards, identified in Table 2, were added to the sample between the heating tube and the mixing chamber at a fixed rate of 1.4 mL·min⁻¹ and the run time was recorded so that the volume of surrogate standards added could be determined.

When there was approximately 1 L of the sample water left in the final carboy, the heater was turned off, the spike feed pump was stopped, and the run time was noted. After all of the sample had passed through the extractor, the water and solvent feed pumps and the stirrer were stopped. The solvent in the bottom of the mixing chamber was drained into a Teflon separatory funnel (used to break up any emulsion). Any solvent remaining in the packed column was brought down into the mixing chamber (and thereafter drained) by draining water out of stopcock B (Fig. 2). The solvent extract was then emptied into 500-mL pre-cleaned round, amber glass bottles, covered with solvent-rinsed (acetone, petroleum ether) aluminum foil, and capped. The water in the extractor was drained into the Teflon separatory funnel and reused to wash the packed column. Any solvent remaining in the system was then collected and added to the amber bottle. All extracts were stored in the dark at 4°C. Blank determinations were made by extracting large samples of reagent-grade water. Analyses were conducted by the National Water Quality Laboratory in Burlington, Ontario.



Figure 6. 1986 Organic contaminant sampling sites on Lake Huron - Georgian Bay.

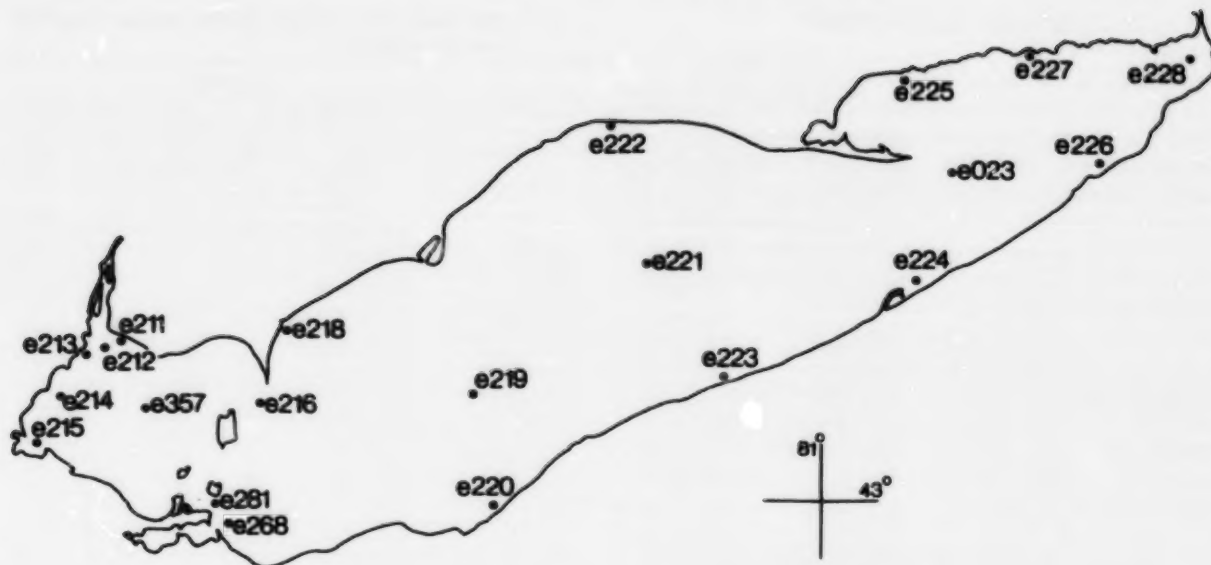


Figure 7. 1986 Organic contaminant sampling sites on Lake Erie.

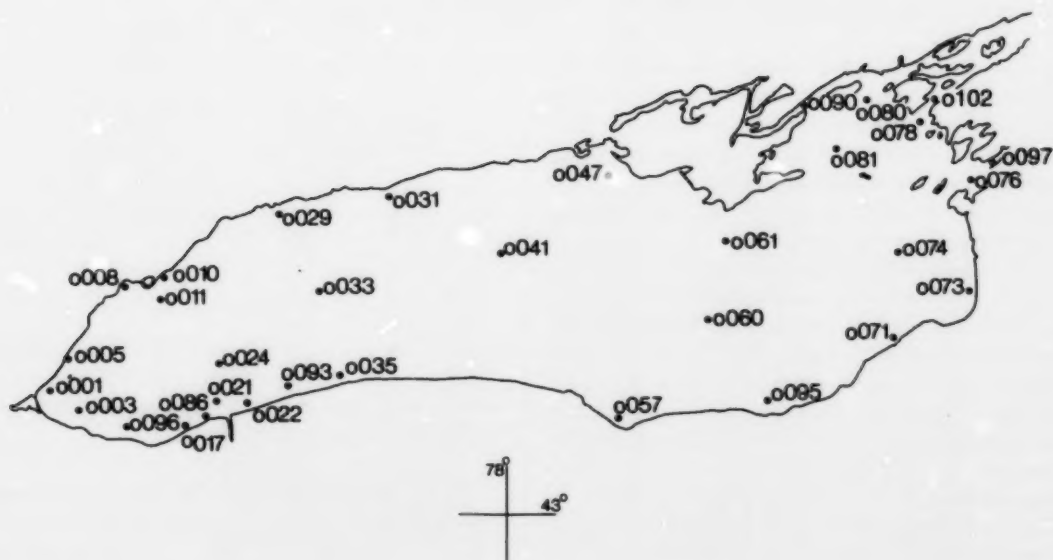


Figure 8. 1986 Organic contaminant sampling sites on Lake Ontario.

RESULTS AND DISCUSSION

Operation of the extractor was basically problem-free and required minimal attention. Run times on the upper Great Lakes, when 66 L was collected, averaged approximately 100 min, whereas on Lake Erie (44 L), run times ranged from approximately 40 to 80 min. In some of the shallower nearshore regions, *in situ* temperatures were as high as 12°C, thereby requiring little heating to bring the sample to room temperature. These samples could thus be run at higher inflow rates.

Only the recoveries of the surrogate materials will be discussed here. Interpretation of the data on natural organic materials will be given in a separate report. Table 3 summarizes, by lake, the recovery data for the five surrogate standards. A listing of the complete data set, by station and lake, is given in Appendix A.

Recovery data for the surrogate standards at each of the stations where centrifuged and ambient duplicates were collected are shown in Figures 9 to 13. There is no indication that either the precision or the accuracy of the recoveries was affected by centrifugation of the sample.

From these results it is clear that there is no evidence that the extractor is obtaining other than complete recovery of the added surrogate materials. Furthermore, analysis of the blanks showed that no detectable levels of any interfering substances were introduced in this process.

It is concluded that the extractor represents a valid pre-concentration process. It should be noted that the recoveries obtained represent that of the complete extraction, clean-up and analytical process. No spikes were made to the solvent after the extraction process, so that it is not possible to assess directly the efficiencies in each process. Since five surrogate standards were used, it is possible to obtain some information on the source of the variability by comparing their ratios before and after the extraction-analysis. The initial ratio of END-KETO:DBB:TBB:TeBB:TCBP in the standard solution was 1:10.3:4.1:4.4:4.5. This ratio was compared with corresponding ratios in the extracts. If the ratios are maintained, it can then be assumed that the variability in recovery efficiency was a result of the extraction procedure. If the ratios vary it would indicate that losses were due to the analytical procedure. Ratios for the extracts (see Appendix B) were normalized to endrin ketone for comparison, since recoveries were generally the most precise for this compound. It would seem that the variability observed in the efficiency of recovery of the surrogates was due to the analytical procedure. Future efforts with the extractor will use a two-stage spiking procedure, one solution to be introduced with the sample

Table 3. 1986 Great Lakes Organics Results: Surrogate Standard Spike Recoveries (%)

Location		Parameters				
		END-KETO	DBB	TBB	TeBB	TCBP
Lake Superior	n	25	25	25	25	25
	$\bar{x}$	102.7	93.5	116.4	116.9	97.6
	S.D.	16.0	17.1	31.1	23.4	14.6
	Min.	75.3	67.9	81.3	85.7	74.1
	Max.	125.3	136.4	177.6	170.9	129.8
	C.V.	15.6	18.3	26.7	20.0	15.0
Lake Huron	n	24	24	24	24	24
	$\bar{x}$	117.0	91.0	113.4	125.6	105.4
	S.D.	24.6	13.1	23.0	31.5	25.1
	Min.	86.0	69.8	83.9	83.5	64.4
	Max.	168.7	115.4	164.2	185.1	149.4
	C.V.	21.0	14.4	20.3	25.1	23.8
Georgian Bay	n	10	10	10	10	10
	$\bar{x}$	115.4	116.6	183.8	174.2	105.1
	S.D.	23.6	16.8	34.4	32.9	25.5
	Min.	93.7	95.3	138.4	133.2	79.8
	Max.	173.5	148.3	253.8	243.8	151.9
	C.V.	20.5	14.4	18.7	18.9	24.2
Lake Erie	n	27	27	27	27	27
	$\bar{x}$	95.1	82.4	91.4	106.8	103.9
	S.D.	28.6	27.4	30.1	37.7	30.4
	Min.	46.8	34.8	37.6	39.4	44.3
	Max.	170.6	118.7	135.7	167.3	147.7
	C.V.	30.1	33.2	33.0	35.3	29.3
Lake Ontario	n	37	37	37	37	36
	$\bar{x}$	91.3	90.1	98.7	107.8	110.9
	S.D.	18.0	17.7	20.9	23.2	23.2
	Min.	50.5	28.1	28.9	31.9	35.8
	Max.	143.0	123.8	138.1	142.9	156.0
	C.V.	19.7	19.6	21.2	21.6	20.9

n - Number of samples.

$\bar{x}$ - Mean percent recovery.

S.D. - Standard deviation.

Min. - Minimum percent recovery.

Max. - Maximum percent recovery.

C.V. - Coefficient of variation.

water, as is presently done, and a different set of standards used to spike the extracts, directly. This will more clearly differentiate between losses due to extraction and losses due to analytical procedures.

In considering design options for a large-sample extractor, one of the advantages of this continuous-flow type of equipment is that it would be comparatively simple to add a solvent-recovery system to the waste water stream (Goulden and Anthony, 1985). With such a system, the waste water would not be a source of contamination to the lake. Furthermore, recovery and recycling of the waste solvent could reduce the amount of solvent used for each

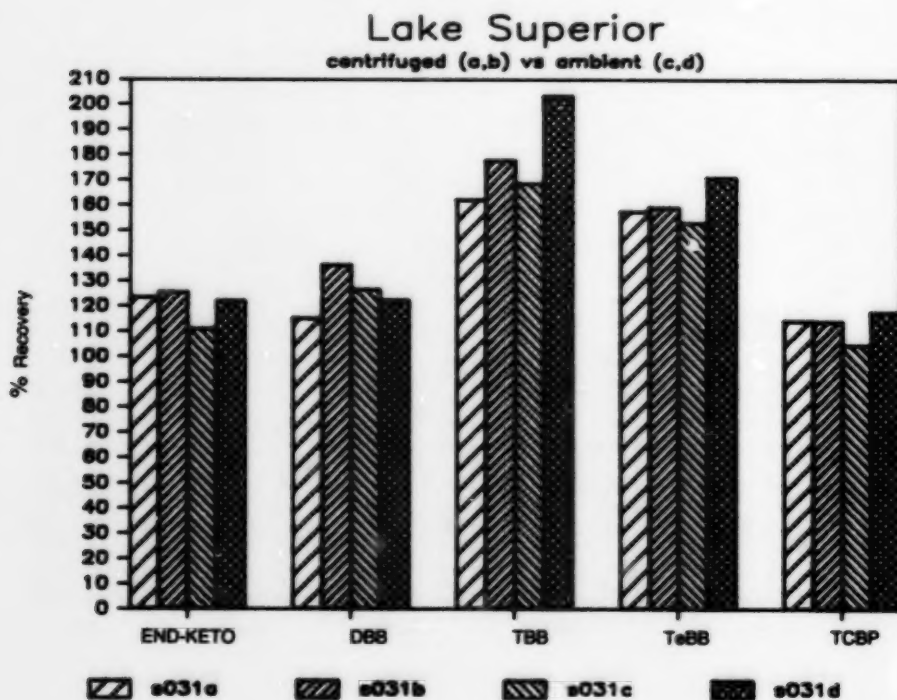
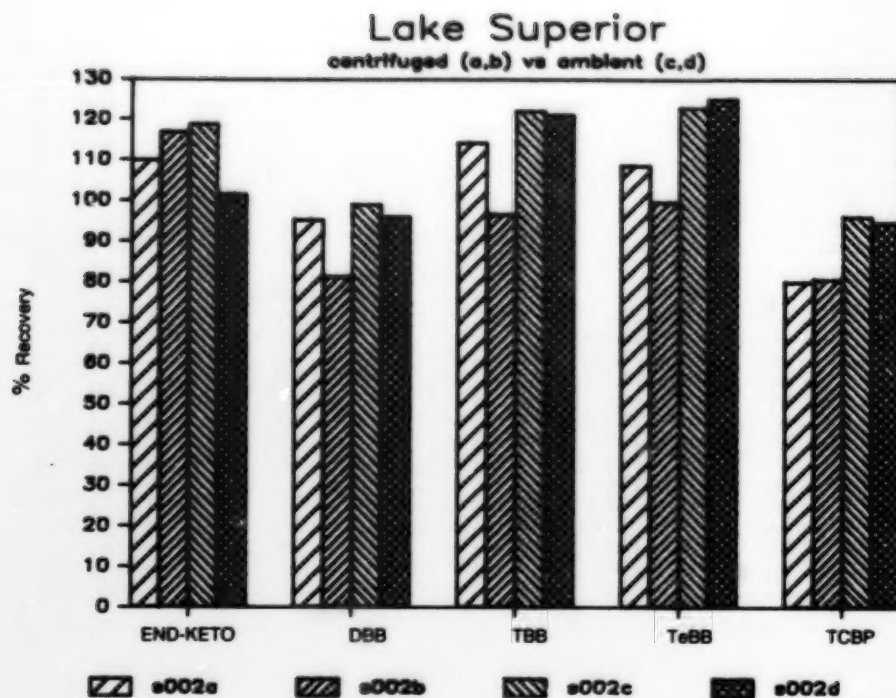


Figure 9. Lake Superior: centrifuged (a,b) vs. ambient (c,d) duplicates.

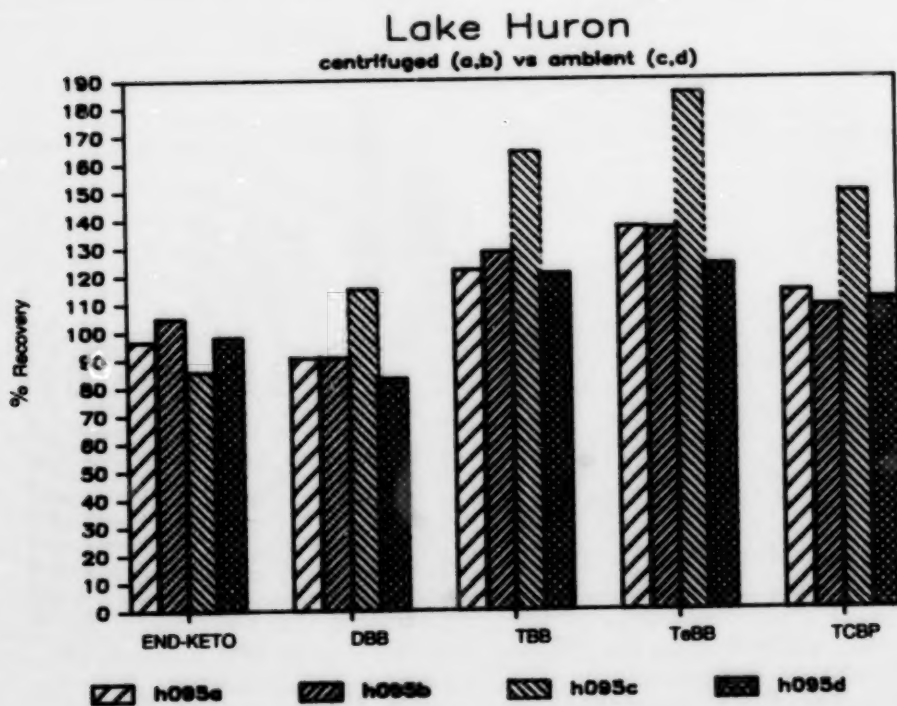
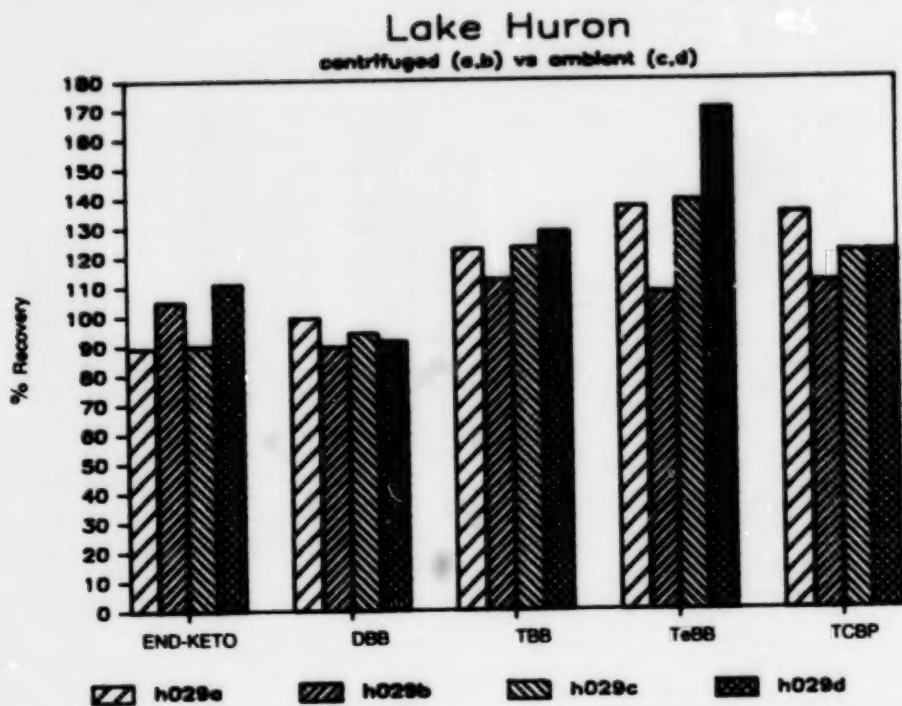


Figure 10. Lake Huron: centrifuged (a,b) vs. ambient (c,d) duplicates.

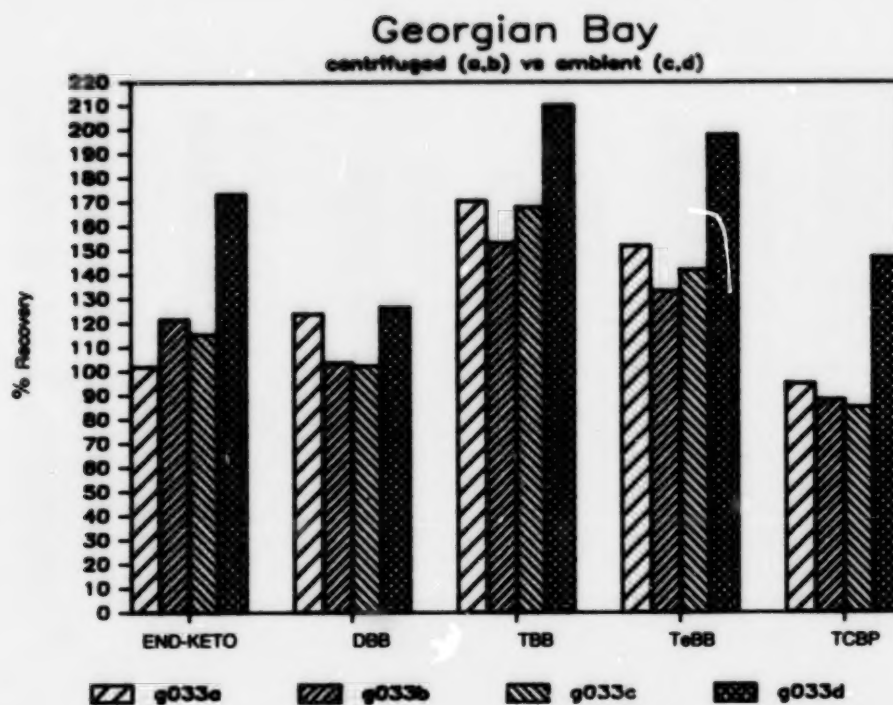


Figure 11. Georgian Bay: centrifuged (a,b) vs. ambient (c,d) duplicates.

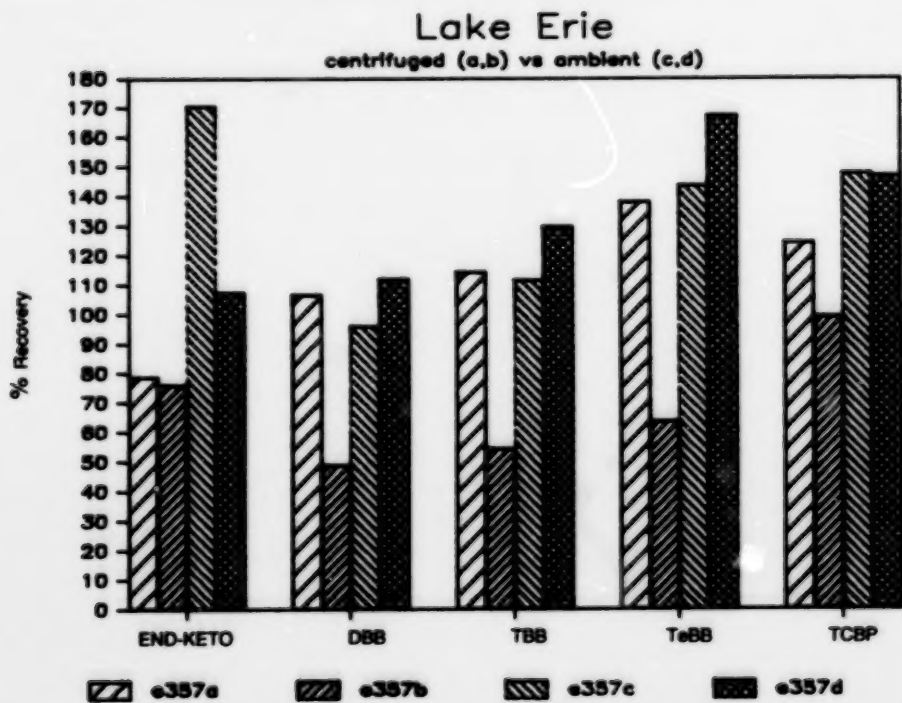
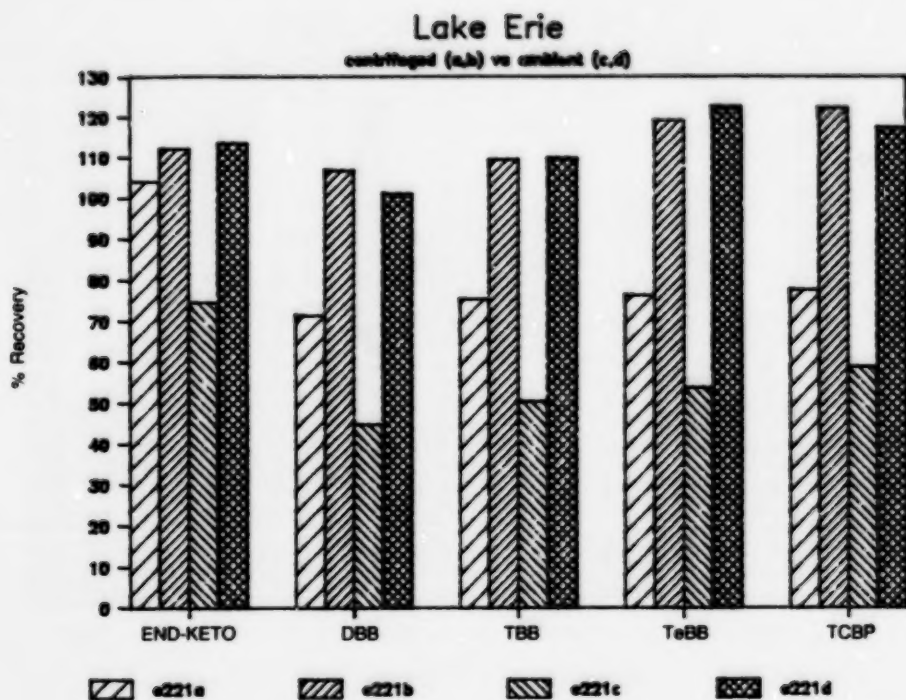


Figure 12. Lake Erie: centrifuged (a,b) vs. ambient (c,d) duplicates.

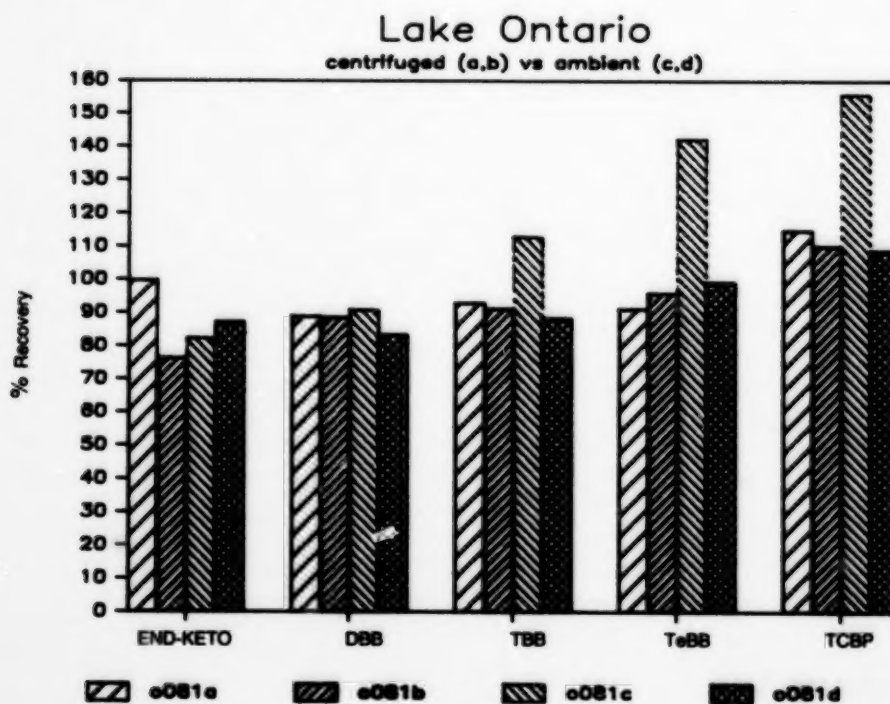
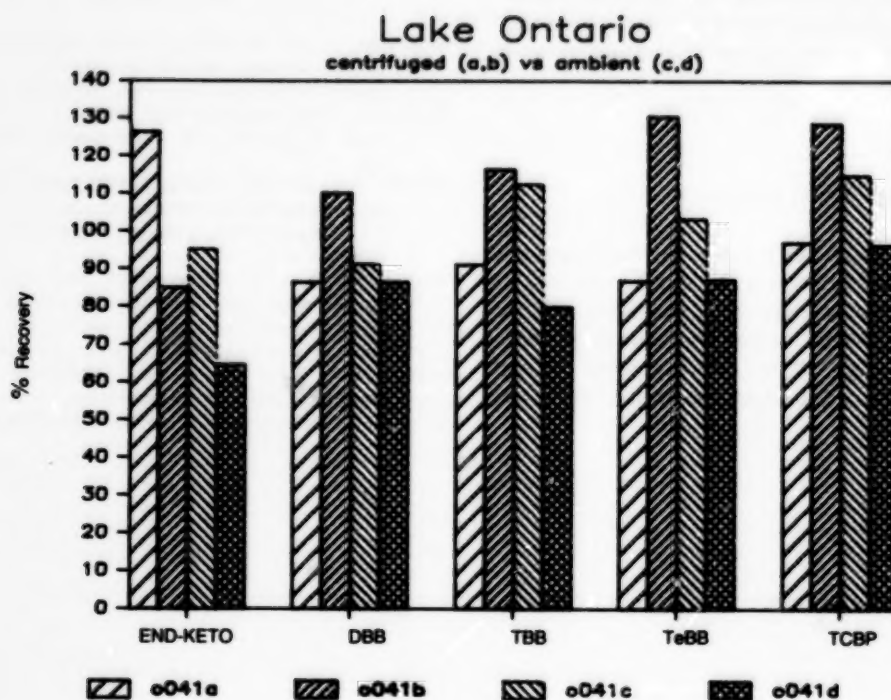


Figure 13. Lake Ontario: centrifuged (a,b) vs. ambient (c,d) duplicates.

extraction by about 75%. Although such a system was not available for the work carried out in this study, it is anticipated that a solvent-recovery system will be used in future work on the Great Lakes.

ACKNOWLEDGMENTS

The authors would like to thank the Ship Operations Division of Technical Operations; the Captain and crew of the CSS *Limnos*; Aline Sylvestre of the Water Quality Branch, and Randy Elliott for their assistance in collecting the samples; and staff of the National Water Quality Laboratory, as well as S. Bachelor, for their diligence and commendable work.

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Appendix A

Table A-1. Percent Recoveries of Surrogate Standards
for Each Station, by Lake

Stn.	END-KETO	DBB	TBB	TeBB	TCBP
e023	86.6	85.4	97.7	123.4	116.3
e211	46.8	66.7	74.7	77.4	76.4
e212	72.7	107.2	114.0	123.3	122.2
e213	79.8	92.3	100.6	113.9	106.1
e214	99.8	38.1	42.8	47.5	47.1
e215	55.6	118.7	135.7	163.2	123.4
e216	62.4	113.7	122.7	134.4	130.3
e218	63.8	105.5	120.1	141.7	127.6
e219	78.1	46.0	50.7	56.7	60.5
e220	71.4	38.7	48.0	63.2	75.6
e221a	104.2	71.6	75.6	76.6	77.9
e221b	112.3	107.1	109.7	119.4	122.6
e221c	74.7	45.0	50.6	54.0	59.1
e221d	113.7	101.3	110.1	122.9	117.6
e222	153.1	82.3	92.6	101.9	105.8
e223	108.1	34.8	37.6	39.4	44.3
e224	93.0	86.2	93.2	105.2	101.4
e225	110.0	98.8	110.1	124.8	120.7
e226	122.1	45.1	49.2	58.9	61.4
e227	105.6	114.1	123.2	146.3	129.3
e228	133.0	99.7	114.4	142.2	140.4
e268	95.4	78.2	86.5	108.9	103.8
e281	92.5	84.5	97.0	126.6	118.8
e357a	78.8	106.6	114.3	138.0	124.2
e357b	76.0	48.9	54.4	63.6	99.1
e357c	170.6	96.0	111.5	143.6	147.7
e357d	107.4	111.9	129.7	167.3	146.8
s002a	110.0	95.3	114.2	108.6	80.0
s002b	116.9	81.2	96.6	99.6	80.6
s002c	118.9	99.0	122.1	122.9	96.2
s002d	101.5	96.0	121.1	125.0	94.7
s031a	123.5	115.2	162.1	157.5	114.2
s031b	125.5	136.4	177.6	159.0	114.0
s031c	111.0	126.7	168.6	153.1	104.8
s031d	122.1	122.4	203.3	170.9	117.6
s089	104.3	90.5	90.0	92.0	77.9
s100	116.8	91.4	112.6	100.8	76.2
s105	103.8	90.7	109.5	108.9	89.9
s113	77.0	77.7	83.4	85.7	87.7
s130	79.7	76.2	100.7	112.5	97.3
s139	98.6	71.4	89.4	113.2	87.4
s140	102.2	84.0	99.8	105.3	106.1
s177	79.7	87.9	100.1	97.3	95.8
s221	94.1	67.9	81.3	93.1	90.7
s220	99.2	83.8	98.5	106.0	108.3
s196	101.2	74.0	91.0	93.4	74.1
s169	119.8	86.4	99.6	103.3	103.8
s164	82.7	103.4	133.6	140.4	119.5
s080	81.7	97.3	116.4	121.4	100.9
s068	120.7	102.9	129.4	136.7	129.8
s051	103.6	90.5	107.3	113.1	101.2

Table A-1. Continued

s023	75.3	88.7	102.4	103.2	91.7
h001	94.2	85.9	138.6	172.6	127.7
h009	94.9	87.0	113.6	128.9	111.9
h017	118.7	75.8	102.4	119.2	93.8
h101	89.3	88.2	135.5	176.4	146.5
h095a	96.8	90.7	122.0	137.2	113.9
h095b	105.1	90.8	128.4	136.6	108.6
h095c	86.0	115.4	164.2	185.1	149.4
h095d	98.3	83.4	120.5	123.7	111.0
h029a	89.5	99.5	122.7	136.8	134.6
h029b	105.2	89.8	112.2	107.8	111.1
h029c	90.3	94.5	123.2	139.0	121.3
h029d	111.1	91.6	128.5	170.1	121.2
h040	151.4	84.8	113.0	138.9	117.3
h036	138.7	101.0	89.3	94.3	85.9
h054	168.7	81.4	102.3	125.1	105.1
h063	166.2	103.1	145.9	100.2	143.4
h064	114.3	76.8	92.3	95.2	76.7
h065	107.0	69.8	81.5	83.5	64.4
h067	123.7	114.2	90.4	96.7	76.7
h076	118.9	103.3	90.1	94.1	80.0
h077	135.5	72.0	83.9	84.8	67.9
h084	150.9	102.6	146.6	170.5	101.1
h071	128.5	110.5	87.6	105.7	88.2
h069	124.8	72.4	87.5	91.7	72.7
g033a	102.2	123.8	170.7	151.9	94.9
g033b	121.6	103.7	153.3	133.2	88.3
g033c	115.6	102.5	168.1	141.9	85.1
g033d	173.5	126.5	210.4	197.9	147.1
g009	130.6	119.5	197.3	177.4	100.6
g001	114.5	148.3	253.8	243.8	151.9
g004	93.7	124.7	195.5	180.7	105.5
g027	108.8	95.3	138.4	158.0	85.3
g029	98.6	125.1	199.3	198.1	112.3
g042	95.3	96.4	151.3	159.1	79.8
o001a	77.8	98.2	93.4	91.9	90.8
o003	91.3	94.8	94.4	109.1	0.0
o005	109.9	102.9	111.1	115.6	116.6
o008	91.8	92.0	104.5	113.5	113.1
o010	82.9	109.1	119.9	128.4	124.1
o011	83.6	99.8	108.5	121.8	125.3
o017	94.1	99.4	114.9	127.9	122.1
o021	107.4	111.0	126.6	133.0	117.6
o022	78.2	111.4	133.0	124.4	112.1
o024	85.8	123.8	138.1	142.9	128.2
o029	75.9	100.4	87.7	108.2	97.1
o031	88.1	103.2	113.8	105.1	92.8
o035	80.4	92.3	100.8	97.1	103.7
o041a	126.5	86.5	91.2	86.9	97.1
o041b	85.1	110.2	116.5	130.6	128.7
o041c	95.4	91.5	112.6	103.5	115.1
o041d	64.8	86.6	80.1	87.4	96.6
o047	67.9	90.5	99.0	119.4	110.8

Table A-1. Continued

o057	109.1	78.3	85.6	105.3	95.3
o060	89.3	84.0	88.7	102.8	102.6
o061	121.8	89.2	96.1	113.4	109.3
o071	105.9	88.6	97.2	122.6	108.5
o073	50.5	36.3	38.7	43.1	48.0
o074	83.1	94.4	99.3	111.5	107.6
o076	67.1	93.4	105.8	136.3	116.5
o078	101.4	28.1	28.9	31.9	35.8
o080	104.7	91.1	100.7	115.3	125.1
o081a	99.9	89.0	93.0	91.3	115.0
o081b	76.4	88.7	91.3	96.0	110.3
o081c	82.5	91.1	113.1	142.4	156.0
o081d	87.4	83.5	88.5	99.4	109.0
o086	96.6	92.0	111.3	133.7	131.8
o090	78.8	80.7	83.0	88.2	83.7
o093	93.6	68.3	84.2	87.9	124.3
o095	108.6	79.2	93.4	103.4	142.8
o096	143.0	89.2	107.7	112.2	138.7
o102	86.8	86.0	98.9	106.2	140.9

Appendix B

Table B-1. Ratios Found in Extracts, Normalized to Endrin Ketone

Stn.	DBB/EK	TBB/EK	TeBB/EK	TCBP/EK
e023	10.1	4.6	6.3	6.0
e211	14.7	6.5	7.3	7.3
e212	15.2	6.4	7.5	7.5
e213	11.9	5.1	6.3	5.9
e214	3.9	1.7	2.1	2.1
e215	21.9	10.0	13.0	9.9
e216	18.7	8.0	9.5	9.3
e218	17.0	7.7	9.8	8.9
e219	6.1	2.6	3.2	3.5
e220	5.6	2.7	3.9	4.7
e221a	7.1	3.0	3.2	3.3
e221b	9.8	4.0	4.7	4.9
e221c	6.2	2.8	3.2	3.5
e221d	9.2	4.0	4.8	4.6
e222	5.5	2.5	2.9	3.1
e223	3.3	1.4	1.6	1.8
e224	9.5	4.1	5.0	4.9
e225	9.2	4.1	5.0	4.9
e226	3.8	1.6	2.1	2.2
e227	11.1	4.8	6.1	5.5
e228	7.7	3.5	4.7	4.7
e268	8.4	3.7	5.0	4.9
e281	9.4	4.3	6.0	5.7
e357a	13.9	5.9	7.7	7.0
e357b	6.6	2.9	3.7	5.8
e357c	5.8	2.7	3.7	3.9
e357d	10.7	4.9	6.9	6.1
s002a	8.9	4.2	4.4	3.2
s002b	7.1	3.4	3.8	3.1
s002c	8.6	4.2	4.6	3.6
s002d	9.7	4.9	5.4	4.2
s031a	9.6	5.4	5.6	4.1
s031b	11.2	5.8	5.6	4.1
s031c	11.7	6.2	6.1	4.2
s031d	10.3	6.8	6.2	4.3
s089	8.9	3.5	3.9	3.3
s100	8.0	3.9	3.8	2.9
s105	9.0	4.3	4.6	3.9
s113	10.4	4.4	4.9	5.1
s130	9.8	5.2	6.2	5.4
s139	7.4	3.7	5.1	4.0
s140	8.4	4.0	4.6	4.6
s177	11.3	5.1	5.4	5.4
s221	7.4	3.5	4.4	4.3
s220	8.7	4.1	4.7	4.9
s196	7.5	3.7	4.1	3.3
s169	7.4	3.4	3.8	3.9
s164	12.9	6.6	7.5	6.4
s080	12.2	5.8	6.6	5.5
s068	8.8	4.4	5.0	4.8
s051	9.0	4.2	4.8	4.4

Table B-1. Continued

s023	12.1	5.5	6.1	5.4
h001	9.4	6.0	8.1	6.0
h009	9.4	4.9	6.0	5.3
h017	6.6	3.5	4.4	3.5
h101	10.2	6.2	8.7	7.3
h095a	9.6	5.1	6.3	5.2
h095b	8.9	5.0	5.7	4.6
h095c	13.8	7.8	9.5	7.7
h095d	8.7	5.0	5.6	5.0
h029a	11.4	5.6	6.8	6.7
h029b	8.8	4.4	4.5	4.7
h029c	10.8	5.6	6.8	6.0
h029d	8.5	4.7	6.8	4.9
h040	5.8	3.0	4.1	3.5
h036	7.5	2.6	3.0	2.8
h054	5.0	2.5	3.3	2.8
h063	6.4	3.6	2.7	3.8
h064	6.9	3.3	3.7	3.0
h065	6.7	3.1	3.4	2.7
h067	9.5	3.0	3.5	2.8
h076	8.9	3.1	3.5	3.0
h077	5.5	2.5	2.8	2.2
h084	7.0	4.0	5.0	3.0
h071	8.8	2.8	3.6	3.1
h069	6.0	2.9	3.2	2.6
g033a	12.5	6.8	6.6	4.1
g033b	8.8	5.1	4.8	3.2
g033c	9.1	5.9	5.4	3.3
g033d	7.5	4.9	5.0	3.8
g009	9.4	6.2	6.0	3.4
g001	13.3	9.0	9.4	5.9
g004	13.7	8.5	8.5	5.0
g027	9.0	5.2	6.4	3.5
g029	13.0	8.2	8.9	5.1
g042	10.4	6.5	7.4	3.7
o001a	13.0	4.9	5.2	5.2
o003	10.7	4.2	5.3	-
o005	9.6	4.1	4.6	4.7
o008	10.3	4.6	5.5	5.5
o010	13.5	5.9	6.8	6.7
o011	12.3	5.3	6.4	6.7
o017	10.9	5.0	6.0	5.8
o021	10.6	4.8	5.5	4.9
o022	14.6	6.9	7.0	6.4
o024	14.8	6.6	7.4	6.7
o029	13.6	4.7	6.3	5.7
o031	12.0	5.3	5.3	4.7
o035	11.8	5.1	5.3	5.8
o041a	7.0	2.9	3.0	3.4
o041b	13.3	5.6	6.8	6.7
o041c	9.9	4.8	4.8	5.4
o041d	13.7	5.0	6.0	6.6
o047	13.7	5.9	7.8	7.3

Table B-1. Continued

o057	7.4	3.2	4.3	3.9
o060	9.7	4.1	5.1	5.1
o061	7.5	3.2	4.1	4.0
o071	8.6	3.7	5.1	4.6
o073	7.4	3.1	3.8	4.2
o074	11.7	4.9	5.9	5.8
o076	14.3	6.4	9.0	7.7
o078	2.8	1.2	1.4	1.6
o080	8.9	3.9	4.9	5.3
o081a	9.2	3.8	4.0	5.1
o081b	11.9	4.9	5.6	6.4
o081c	11.4	5.6	7.6	8.4
o081d	9.8	4.1	5.0	5.6
o086	9.8	4.7	6.1	6.1
o090	10.5	4.3	4.9	4.7
o093	7.5	3.7	4.2	5.9
o095	7.5	3.5	4.2	5.9
o096	6.4	3.1	3.5	4.3
o102	10.2	4.7	5.4	7.2

Table B-1. Continued

s023	12.1	5.5	6.1	5.4
h001	9.4	6.0	8.1	6.0
h009	9.4	4.9	6.0	5.3
h017	6.6	3.5	4.4	3.5
h101	10.2	6.2	8.7	7.3
h095a	9.6	5.1	6.3	5.2
h095b	8.9	5.0	5.7	4.6
h095c	13.8	7.8	9.5	7.7
h095d	8.7	5.0	5.6	5.0
h029a	11.4	5.6	6.8	6.7
h029b	8.8	4.4	4.5	4.7
h029c	10.8	5.6	6.8	6.0
h029d	8.5	4.7	6.8	4.9
h040	5.8	3.0	4.1	3.5
h036	7.5	2.6	3.0	2.8
h054	5.0	2.5	3.3	2.8
h063	6.4	3.6	2.7	3.8
h064	6.9	3.3	3.7	3.0
h065	6.7	3.1	3.4	2.7
h067	9.5	3.0	3.5	2.8
h076	8.9	3.1	3.5	3.0
h077	5.5	2.5	2.8	2.2
h084	7.0	4.0	5.0	3.0
h071	8.8	2.8	3.6	3.1
h069	6.0	2.9	3.2	2.6
g033a	12.5	6.8	6.6	4.1
g033b	8.8	5.1	4.8	3.2
g033c	9.1	5.9	5.4	3.3
g033d	7.5	4.9	5.0	3.8
g009	9.4	6.2	6.0	3.4
g001	13.3	9.0	9.4	5.9
g004	13.7	8.5	8.5	5.0
g027	9.0	5.2	6.4	3.5
g029	13.0	8.2	8.9	5.1
g042	10.4	6.5	7.4	3.7
o001a	13.0	4.9	5.2	5.2
o003	10.7	4.2	5.3	-
o005	9.6	4.1	4.6	4.7
o008	10.3	4.6	5.5	5.5
o010	13.5	5.9	6.8	6.7
o011	12.3	5.3	6.4	6.7
o017	10.9	5.0	6.0	5.8
o021	10.6	4.8	5.5	4.9
o022	14.6	6.9	7.0	6.4
o024	14.8	6.6	7.4	6.7
o029	13.6	4.7	6.3	5.7
o031	12.0	5.3	5.3	4.7
o035	11.8	5.1	5.3	5.8
o041a	7.0	2.9	3.0	3.4
o041b	13.3	5.6	6.8	6.7
o041c	9.9	4.8	4.8	5.4
o041d	13.7	5.0	6.0	6.6
o047	13.7	5.9	7.8	7.3

Table B-1. Continued

o057	7.4	3.2	4.3	3.9
o060	9.7	4.1	5.1	5.1
o061	7.5	3.2	4.1	4.0
o071	8.6	3.7	5.1	4.6
o073	7.4	3.1	3.8	4.2
o074	11.7	4.9	5.9	5.8
o076	14.3	6.4	9.0	7.7
o078	2.8	1.2	1.4	1.6
o080	8.9	3.9	4.9	5.3
o081a	9.2	3.8	4.0	5.1
o081b	11.9	4.9	5.6	6.4
o081c	11.4	5.6	7.6	8.4
o081d	9.8	4.1	5.0	5.6
o086	9.8	4.7	6.1	6.1
o090	10.5	4.3	4.9	4.7
o093	7.5	3.7	4.2	5.9
o095	7.5	3.5	4.2	5.9
o096	6.4	3.1	3.5	4.3
o102	10.2	4.7	5.4	7.2